DARTMOUTH COLLEGE
LIBRARY

VOL. XV. 3. MARCH, 1862.

THE

JOURNAL

OF

THE CHEMICAL SOCIETY.

Committee of Publication.

E. FRANKLAND, PH.D., F.R.S. | W. ODLING, M.B., F.R.S.
A. W. HOFMANN, LL.D., F.R.S. | A. W. WILLIAMSON, PH.D., F.R.S.

Editor:

HENRY WATTS, B.A., F.C.S.

N° LIX.

LONDON:
HIPPOLYTE BAILLIERE, 219, REGENT STREET.
1862.

Price One Shilling.

LONDON: PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W. C.

CHEMICAL SOCIETY.

Officers and Council.

Elected March 30, 1861.

PRESIDENT.

A. W. HOFMANN, LL.D., F.R.S.

VICE-PRESIDENTS,

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

W. T. BRANDE, F.R.S.
B. C. BRODIE, F.R.S.
C. G. B. DAUBENY, M.D., F.R.S.
THOMAS GRAHAM, F.R.S.
W. A. MILLER, M.D., F.R.S.
LYON PLAYFAIR, PH.D., C.B., F.R.S.
COLONEL PHILIP YORKE, F.R.S.

VICE-PRESIDENTS.

H. BENCE JONES, M.D., F.R.S.
ROBERT PORRETT, F.R.S.
ALFRED SMEE, F.R.S.
A. W. WILLIAMSON, PH.D., F.R.S

SECRETARIES.

THEOPHILUS REDWOOD, PH.D.
WILLIAM ODLING, M.B., F.R.S.

FOREIGN SECRETARY.

E. FRANKLAND, PH.D., F.R.S.

TREASURER.

WARREN DE LA RUE, PH.D., F.R.S.

OTHER MEMBERS OF THE COUNCIL.

THOMAS ANDREWS, M.D., F.R.S.
WILLIAM FRANCIS, PH.D., F.L.S.
J. H. GLADSTONE, PH.D., F.R.S.
G. D. LONGSTAFF, M.D.
W. MARCET, M.D., F.R.S.
JOHN MERCER, F.R.S.
A. R. NORMANDY, ESQ.
W. H. PERKIN, ESQ.
H. E. ROSCOE, PH.D.
EDWARD SCHUNCK, PH.D.
JOHN STENHOUSE, LL.D., F.R.S.
R. WARINGTON, ESQ.

LIBRARIAN.

HENRY WATTS, B.A., F.C.S.

COLLECTOR.

MR. THOMAS WEST, BURLINGTON HOUSE.

XVI.—*On the Simultaneous Variations of Hippuric and Uric Acids in Healthy Urine.*

By H. Bence Jones, M.D., F.R.S.

In *Henle's Zeitschrift für rationelle Medicin*, 1858, ii., 331, Dr. A. Weismann gives the results of his experiments on the amount of hippuric acid in healthy urine These results were obtained by evaporating very small quantities (20 cc.) of urine, and they show so large an amount of hippuric acid excreted daily, that a different method of analysis seemed most desirable. The average amount excreted during four days of mixed diet he gives as 40·6 grs. daily.

M. Wreden, in the *Bulletin de St. Petersburg, Classe Phys.-med.* xvii., 500, states that he determined the amount of hippuric acid in healthy urine by means of a standard solution of chloride of iron; the amount he obtained was also immense.

He gives, as the mean of twenty-nine determinations, 47·4 grs. of hippuric acid to a litre (1000 cc.) of urine = 1·7 pint. The minimum amount found was 32·3 grs., and the maximum 87·8 grs. to a litre.

In the following experiments, the method of determining hippuric acid, described by Professor Liebig, in the *Annalen der Chemie und Pharmacie*, vol. 50, p. 170, was followed, as being the most accurate, provided a sufficient quantity of urine is taken for analysis and sufficient ether is used. Usually 400 cc. of urine were evaporated to a syrupy consistence in a water-bath; hydrochloric acid was added, and the hippuric acid was extracted by treating the precipitate with ether four or five times. That by this method results are obtained which agree very well together, the following experiments show:

840 cc. of urine were divided into two equal parts, and the amount of hippuric acid in each part was determined.

Weight of hippuric acid, 1st experiment, 3·53 grs.; 2nd experiment, 3·42 grs.

700 cc. were divided into two equal parts and the hippuric acid was determined in each.

Weight of hippuric acid, 1st experiment, 1·49 gr.; 2nd experiment, 1·42 gr.

The determination of the amount of uric acid in all the following experiments (except in experiments 13, 14, 15, 16), was made after the hippuric acid had been extracted by ether. The syrupy residue was then diluted with a little water, and filtered 24 hours afterwards. The uric acid was dissolved in soda, precipitated by hydrochloric acid, and collected 24 hours afterwards.

In experiments 13, 14, 15, and 16, a separate quantity of urine was taken, to which hydrochloric acid was added, and after standing 24 hours, the uric acid was collected on a filter.

Two healthy men were the subjects of the experiments.

The diet of A, who weighed 10st. 12lbs., was, breakfast (8½ a.m.) tea, bread and butter; luncheon (1 p.m.) bread and butter; dinner (5½ p.m.) a pound and a-half of meat, bread and tea; supper (9 p.m.) bread and cheese, and pint of beer. Moderate exercise was taken.

The diet of B, weighing 14st. 6lbs., was, breakfast (9 a.m.) about ⅔ pound of meat, bread, butter, and tea; dinner (7 p.m.) about one pound of meat and some vegetables, with brandy and water or tea. Very little exercise was taken.

Firstly, experiments were made on the total quantity of hippuric acid excreted in 24 hours.

A. The total amount of urine passed in 24 hours was 930 cc.; sp. gr. 1022. 400 cc. were taken for the determination of the hippuric acid. The uric acid was lost by accident.

Weight of hippuric acid 2·64 grs. Hence 930 cc. contained hippuric acid 6·1 grs.

A. The total amount of urine passed in 24 hours was 980 cc.; sp. gr. 1020. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid, 1·68 gr.; weight of the uric acid, 3·44 grs. Hence the 980 cc. contain hippuric acid 4·1 grs.; uric acid 8·4 grs.

A. The total amount of urine passed in 24 hours was 790 cc.; sp. gr. 1022.

Weight of hippuric acid 2·42 grs.; weight of uric acid 3·60 grs. Hence the 790 cc. contain hippuric acid 4·7 grs.; uric acid 7·1 grs.

Hence the daily excretion of A in the three experiments was:

	1st.	2nd.	3rd.	Mean.
Hippuric acid .	6·1 grs.	4·1 grs.	4·7 grs.	4·9 grs.
Uric acid . .	—	8·4 grs.	7·1 grs.	7·7 grs.

B. The total amount of urine passed by B in 24 hours was 1460 cc.; sp. gr. 1017. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid 2·00 grs.; weight of uric acid 4·00 grs. Hence the 1460 cc. contain hippuric acid 7·3 grs.; uric acid 14·6 grs.

B. The total amount of urine passed in 24 hours was 1103 cc.; sp. gr. 1019.

Weight of hippuric acid, 1st experiment, 2·00 grs.; 2nd experiment, 2·12 grs. Weight of uric acid, 1st experiment, 3·95 grs.; 2nd experiment, 4·00 grs.

Hence the 1103 cc. contain—

	1st exp.	2nd exp.	Mean.
Hippuric acid .	5·5 grs.	5·8 grs.	5·65 grs.
Uric acid . .	10·8 grs.	11·0 grs.	10·9 grs.

B. The total amount of urine passed in 24 hours was 1510 cc.; sp. gr. 1017. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid, 1st experiment, 1·98 gr.; 2nd experiment, 2·08 grs. Weight of uric acid, 1st experiment, 3·46 grs.; 2nd experiment, 3·54 grs. Hence the 1510 cc. contain—

	1st exp.	2nd exp.	Mean.
Hippuric acid .	7·45 grs.	7·8 grs.	7·6 grs.
Uric acid . .	13·0 grs.	13·3 grs.	13·1 grs.

B. The total amount of urine passed in 24 hours was 1326 cc.; sp. gr. 1019. 400 cc. were taken for the determination of the hippuric acid.

Weight of hippuric acid 1·76 gr.; weight of uric acid 3·80 grs. Hence the 1326 cc. contain hippuric acid 5·8 grs.; uric acid 12·5 grs.

Hence the daily excretion of B in the four experiments was—

	1st.	2nd.	3rd.	4th.	Mean.
Hippuric acid	7·3 grs.	5·6 grs.	7·6 grs.	5·8 grs.	6·5 grs.
Uric acid	14·6 grs.	10·9 grs.	13·1 grs.	12·5 grs.	12·6 grs.

Secondly, to determine the variations in the amount of hippuric and uric acids in the urine, passed before and after food, a long series of experiments were made with the urine of B.

In the following four experiments 400 cc. of urine passed before and after food were taken:

Experiment 1.—Before food, sp. gr. 1016; weight of hippuric acid 1·52 gr.; weight of uric acid 2·70 grs. After food, sp. gr. 1018; weight of hippuric acid 2·70 grs.; weight of uric acid 4·64 grs.

Experiment 2.—Before food, sp. gr. 1013; weight of hippuric acid 1·10 gr.; weight of uric acid, 2·80 grs. After food, sp. gr. 1019; weight of hippuric acid 1·94 gr.; weight of uric acid 4·78 grs.

Experiment 3.—Before food, sp. gr. 1016; weight of hippuric acid 1·12 gr.; weight of uric acid 3·46 grs. After food, sp. gr. 1019; weight of hippuric acid 3·88 grs.; weight of uric acid 5·32 grs.

Experiment 4.—Before food, sp. gr. 1013; weight of hippuric acid 1·34 gr.; weight of uric acid 1·92 gr. After food, sp. gr. 1018; weight of hippuric acid 3·60 grs.; weight of uric acid 3·00 grs.

In the next six experiments 350 cc. of urine were taken:

Experiment 5.—Before food, sp. gr. 1014; weight of hippuric acid 1·46 gr.; weight of uric acid 2·62 grs. After food, sp. gr. 1016; weight of hippuric acid 1·94 grs.; weight of uric acid 3·80 grs.

Experiment 6.—Before food, sp. gr. 1012; weight of hippuric acid 2·02 grs.; weight of uric acid 0·68 gr. After food, sp. gr. 1012; weight of hippuric acid 1·20 gr.; weight of uric acid 2·04 grs.

Experiment 7.—Before food, sp. gr. 1019; weight of hippuric acid 2·04 grs.; weight of uric acid 3·43 grs. After food, sp. gr. 1014; weight of hippuric acid 2·84 grs.; weight of uric acid 2·84 grs.

Experiment 8.—Before food, sp. gr. 1012; weight of hippuric acid 1·12 gr.; weight of uric acid 1·14 gr. After food, sp. gr. 1013; weight of hippuric acid 1·62 gr.; weight of uric acid 2·24 grs.

Experiment 9.—Before food, sp. gr. 1019; weight of hippuric acid 1·44 gr.; weight of uric acid 1·90 gr. After food, sp. gr. 1·017; weight of hippuric acid 1·97 gr.; weight of uric acid 2·30 grs.

Experiment 10.—Before food, sp. gr. 1012; weight of hippuric acid 1·01 gr.; weight of uric acid 0·10 gr. After food, sp. gr. 1016; weight of hippuric acid 1·01 gr.; weight of uric acid 1·88 gr.

Experiment 11.—375 cc. of urine passed before and after food

were taken. Before food, sp. gr. 1020; weight of hippuric acid 1·41 gr.; weight of uric acid 2·92 grs. After food, sp. gr. 1016: weight of hippuric acid 1·18 gr.; weight of uric acid 2·94 grs.

Experiment 12.—Before food, sp. gr. 1022; weight of hippuric acid 1·36 gr.; weight of uric acid 2·56 grs. After food, sp. gr. 1025; weight of hippuric acid 1·94 gr.; weight of uric acid 4·92 grs.

Experiment 13.—570 cc. of urine passed before and after food were taken for the determination of the hippuric acid; and 190 cc. of urine passed before and after food were taken for the determination of the uric acid. Before food, sp. gr. 1014; weight of hippuric acid 1·20 gr.; weight of uric acid in 190 cc. 0·61 gr.; ditto, in 570 cc. 1·83 gr. After food, sp. gr. 1015; weight of hippuric acid 2·02 grs.: weight of uric acid in 190 cc. 1·32 gr.; ditto, in 570 cc. 3·96 grs.

Experiment 14.—380 cc. of urine passed before food were taken for the determination of the hippuric acid, and 240 cc. for uric acid. 380 cc. of urine passed after food were taken for the determination of both. Before food, weight of hippuric acid 3·80 grs.; weight of uric acid in 240 cc. 2·26 grs; ditto, in 380 cc. 3·50 grs. After food, weight of hippuric acid 2·26 grs.; weight of uric acid in 380 cc. 4·60 grs.

Experiment 15.—300 cc. of urine passed before food were taken for the determination of the hippuric acid, and 200 cc. for uric acid; 300 cc. of urine passed after food were taken for the determination of both. Before food, weight of hippuric acid 2·00 grs.; weight of uric acid in 200 cc. 1·20 gr.; ditto, in 300 cc. 1·80 gr. After food, weight of hippuric acid 1·18 gr.; weight of uric acid in 300 cc. 2·30 grs.

Experiment 16.—127 cc. of urine were taken before food for the determination of the hippuric and uric acids, and 150 cc. of urine were taken after food for the determination of the hippuric and uric acids. Before food, weight of hippuric acid in 127 cc. 1·01 gr.; weight of uric acid in 127 cc. 1·24 gr. After food, weight of hippuric acid in 150 cc. 1·10 gr.; ditto, in 127 cc., 0·93 gr.; weight of uric acid in 150 cc. 1·68 gr.; ditto, 127 cc., 1·42 gr.

Experiment 17.—400 cc. of urine were taken before food for the determination of the hippuric and uric acids, and 244 cc. of urine were taken after food for the determination of the hippuric and uric acids. Before food, sp. gr. 1013; weight of hippuric acid in 400 cc. 1·80 gr.; weight of uric acid in 400 cc. 2·54 grs. After

food, sp. gr. 1023; weight of hippuric acid in 244 cc. 3·00 grs.; ditto, in 400 cc. 4·90 grs.; weight of uric acid in 244 cc. 3·78 grs.; ditto, in 400 cc., 6·19 grs.

Hence, there were in 1000 cc. of urine before food, and in 1000 cc. of urine after food,—

	Before Food.			After Food.		
Exp.		Sp. Gr.	Grs.	Sp. Gr.	Grs.	
1.	Hippuric acid	1016	3·8 ..	1018	6·7	hippuric acid
	Uric „	„	6·8 ..	„	11·6	uric „
2.	Hippuric „	1013	2·7 ..	1019	4·8	hippuric „
	Uric „	„	7·0 ..	„	11·9	uric „
3.	Hippuric „	1016	2·8 ..	1019	9·7	hippuric „
	Uric „	„	8·6 ..	„	13·3	uric „
4.	Hippuric „	1013	3·3 ..	1018	9·0	hippuric „
	Uric „	„	4·8 ..	„	7·5	uric „
5.	Hippuric „	1014	4·1 ..	1016	5·5	hippuric „
	Uric „	„	7·4 ..	„	10·8	uric „
6.	Hippuric „	1012	5·7 ..	1012	3·4	hippuric „
	Uric „	„	1·9 ..	„	5·7	uric „
7.	Hippuric „	1019	5·8 ..	1014	8·1	hippuric „
	Uric „	„	9·8 ..	„	8·1	uric „
8.	Hippuric „	1012	3·2 ..	1013	4·5	hippuric „
	Uric „	„	3·2 ..	„	6·4	uric „
9.	Hippuric „	1019	4·1 ..	1017	5·6	hippuric „
	Uric „	„	4·2 ..	„	6·5	uric „
10.	Hippuric „	1012	2·8 ..	1016	2·8	hippuric „
	Uric „	„	0·2 ..	„	5·3	uric „
11.	Hippuric „	1020	3·7 ..	1016	3·1	hippuric „
	Uric „	„	7·7 ..	„	7·8	uric „
12.	Hippuric „	1022	3·6 ..	1025	5·1	hippuric „
	Uric „	„	6·8 ..	„	13·1	uric „
13.	Hippuric „	1014	2·1 ..	1015	3·5	hippuric „
	Uric „	„	3·2 ..	„	6·9	uric „
14.	Hippuric „	„	10·0 ..	„	5·9	hippuric „
	Uric „	„	9·4 ..	„	12·1	uric „
15.	Hippuric „	„	6·6 ..	„	3·9	hippuric „
	Uric „	„	6·0 ..	„	7·6	uric „
16.	Hippuric „	„	7·9 ..	„	7·3	hippuric „
	Uric „	„	9·7 ..	„	11·2	uric „
17.	Hippuric „	1013	4·5 ..	1023	12·2	hippuric „
	Uric „	„	6·3 ..	„	15·4	uric „

Hence the average, in 1000 cc. of urine before food, is—sp. gr. of urine 1015·3—hippuric acid 4·51 grs; uric acid 6·05 grs. After food, sp. gr. 1017·2; hippuric acid 5·94 grs.; uric acid 9·48 grs.

It follows, from these two series of experiments on the quantity of hippuric and uric acid excreted in twenty-four hours, and on the increase or diminution of the hippuric and uric acids in the urine after food, that in 24 hours:—

1. The lighter man gave 4·96 grs. of hippuric acid
and 4·74 grs. of uric acid;
the mean quantity of urine being 1·25 pints.

The heavier man gave 6·5 grs. of hippuric acid
and 11·6 grs. of uric acid;
the mean quantity of urine being 2·37 pints.

2. The hippuric acid was increased, on an average, in the heavier man } from 4·51 grs. per 1000 cc. urine before food to 5·94 grs. „ „ after food

Whilst the uric acid was increased on an average } from 6·05 grs. „ „ before food to 9·45 grs. „ „ after food

Liebig states,* that all the urine that he examined of persons living on mixed diet contained about equal quantities of hippuric and uric acid.

Parkes, in his work, "On the Composition of the Urine," p. 12, gives the amount of uric acid found by fourteen observers in the urine secreted in 24 hours. The lowest quantity was 4·32 grs., and the highest 14·49 grs. The mean of all the observations together was 8·5 grs. of uric acid in 24 hours.

As yet I have made only a very few experiments on the amount of hippuric acid present in the urine in diseased states of the body.

Bouchardat, in the "Annuaire de Thérapeutique" for 1842, p. 285, speaks of a disease which he calls "hippurie." A case resembling his description was met with in St. George's Hospital. The urine was very dilute, of yellowish colour, and feebly alkaline reaction. 420 cc. of urine contained only traces of hippuric acid.

In a case of acute rheumatic fever, the sp. gr. of the urine was

* Ann. Ch. Pharm. 50, p. 170.

1010; it had a brown yellow colour and acid reaction. 350 cc. of this urine contained a very small quantity of hippuric acid.

In a case of diabetes (sp. gr. of the urine 1040), 400 cc. of urine were examined for hippuric acid, but only traces were found.

These experiments only show that a far more extended inquiry is requisite to find the variations of hippuric acid in disease.

In conclusion, I must express my obligation to Dr. Ulrich for the care he took to make these results as accurate as possible.

XVII.—*On Ground Ice.*

By Richard Adie, Liverpool.

In a note to the paper on this subject which I last year submitted to the Chemical Society, Dr. Frankland has referred to the phenomenon of ground ice, as well known to take place in rapidly flowing streams, and as having for its origin a source which I imagine to be similar to that adduced by M. Arago, in his paper on this question in the "Annuaire" for 1833, namely, "the aptitude to the formation of crystals of ice on stones and asperities of the bottom cooled to 32° F."

I wish to return to the subject to state that the district where ground ice is to be found very much more frequently than in any other place with which I am acquainted, is called "Altcar," about 11 miles north of Liverpool. Here I have found it twice during two moderate frosts of the present month of January, 1862. The country there is flat, with wide, slow-flowing ditches separating the fields, and no hedge-rows or fences. Here two nights' moderate frost appear to be sufficient to cool down the water on the surface of these ditches to near 32° F. When this occurs, there is a supply of ice-crystals, derived chiefly from a fringe of them along the edges, which are seen to be continually detached and floated down with the current. Now, it is to these crystals that I attribute the lodgments of ice: for they are found in the places most suited to their detention, without any reference to the exposure of the surface—for example, where a stream sweeps round a turn or corner, the weeds or plants there are sure to be the first to contain submerged ice.

On the surface there is a supply of asperities for the formation of crystals at the edges more than at any other part of the stream; and, as the temperature is often ten degrees lower at the surface than it can be under water, this view of the question is in accordance with all the observed facts.

On the 1st of January, I examined a stream, locally known by the name of "The Brook," a tributary of the river Alt, and found ice on the plants in the bed of the stream at places favourable to its detention; some of it had a soiled aspect, and contained many air-bubbles, giving evidence of two or three days age. The frost was of a mild character, but of several days' duration. Surface ice on stagnant pools was trustworthy to walk on only where the water was shallow.

On the 22nd of January I again visited the Altcar district, after a second frost of a few days' duration had been established. At this time, the thermometer had ranged six to eight degrees below 32° on the Fahrenheit scale, accompanied by a brisk, piercing wind. There was abundance of ground ice in the tributary, and also in the river Alt, where I had not before found it. In some parts, where on former occasions ground ice had been plentiful, at the present time surface ice covered everything; but it showed that, while forming, it had received large supplies of the ground ice. This I particularly remarked around and under the arch of a narrow bridge, where a quantity of spherical-shaped masses, such as collect on the plants that twist and turn in the bed of a stream, had been floated into a mass stretching across the surface, and there frozen into strong ice.

I remember having seen a remark that in some districts ground ice is a characteristic of the beginning of a frost, of which the above observation gives a confirmation; and I have no doubt that a quick, sharp frost would cover the waters in Altcar with surface ice, to the exclusion of the formation of ground ice, but I have not been in the neighbourhood on such an occasion to examine them.

The early period of the winter at which it has been recorded that ground ice was abundant, is another proof that it belongs to the beginning of a frost. A friend of mine wrote from Hawick, under date 17th November, 1841, that he had seen ground ice in abundance in the river Teviot. This fact of ground ice making its appearance at the early part of a frost, strongly favours the view that it is derived from edge-formed crystals: for this is the place where on every occasion the ice will first form.

Dr. Farquharson, who described the ground ice in the ditches of Lincolnshire, in the "Transactions of the Royal Society," appears to have had a district as favourable for showing it as Altcar.

The reason why streams of a flat country are so much more quickly cooled to near the freezing point than those of a more uneven surface is, that they are free from underground supply, either from natural or artificial sources. I can remember examining a slow-flowing stream which received the water of many tile drains; this, during a severe frost, ran in the centre as clear as in a midsummer day, with only a light fringe of ice crystals along the edges.

In the valley of the Tay, and some of the northern rivers of the island, the people resident say that a frozen fog is a freqent precursor of ground ice. While examining the Altcar ground on the 1st of January, I had a palpable proof of the immense quantity of ice-crystals a wooded district would supply to a stream running underneath the branches of the trees. The weather at the close of the year was foggy, the night frosts covering wooded districts with beautiful displays of ice-foliage. For two or three successive days, the sun's rays had power so far to relax the frost that the ice fell from the branches to the frozen ground. When on the ground the ice did not melt much. The branches were thus daily prepared to receive a fresh supply from the frosty and foggy night air. In this manner a large quantity of ice-crystals had collected in the shade of every tree, and these, be it observed, were more available for ground ice in a stream than if they had been supplied by snow, for in the latter case the surrounding country is covered, and the streams receive water as if from drains.

Some years ago, when I first examined ice in the beds of streams, I held the opinion that the temperature of 32° was indispensable for its appearance and preservation. From more recent experiments, I am of opinion that the ground ice may be preserved and be lodged with the water of the stream from three to five-tenths of a degree of Fahrenheit above the freezing point, when the temperature of the external atmosphere is low enough to form ice-crystals at the surface along the edges.

XVIII.—*On the occurrence of considerable Deposits of Crystallized Phosphate of Lime in Teak-wood.*

By F. A. Abel, F.R.S.

The wood of the *Tectona grandis*, which is imported from the south of India and a few other tropical countries, has been very extensively employed within the last few years in connexion with military equipments (for example, in the construction of gun-carriages, packing cases, &c.), required for use in tropical climates, as it is greatly superior to other descriptions of wood in its power of resisting the destructive effects of extreme changes of temperature.

In the reduction of the large blocks of teak-wood to planks and small timber, deposits of a white substance, sometimes soft and pulverulent, at other times so hard as quickly to blunt the cutting edges of the saws employed, are constantly met with, intersecting the wood in the form of layers converging towards the centre or heart of the tree, from which point they usually start. These layers or deposits are often several feet in length (some have been found to extend more than six feet), and measure six or eight inches in breadth, the thickness of the layers varying from one-eighth to three-eighths of an inch. Where these layers occur, they have evidently been gradually deposited in flaws or cracks (so called shakes), which have formed in the living tree. Cavities, occasioned by knots in the wood are frequently lined or filled with the same white deposit; as are also the perforations, of considerable size and length, which are constantly met with in the teak-wood, and which owe their existence to the labours of a large caterpillar. The remains of huge moths into which these insects have become transformed, are occasionally found in the wood; the bodies of these consist of a ceraceous substance, which on examination was found to exhibit the general properties of the product of the long-continued action of moisture upon fatty matters, known as adipocere.

The white deposit, the occurrence of which has just been described, exhibits occasionally a very distinct striated crystalline structure, and sometimes consists of conglomerates of small acicular crystals, easily distinguished by the aid of a microscope of low power. It is readily soluble in dilute acids, with separation of a very small quantity of organic colouring matter. Effer-

vescence is not generally observable on dissolving the substance, but on the application of a very gentle heat to the solution, a minute quantity of carbonic acid gas is disengaged.

The analysis of an average specimen of this deposit, dried in *vacuo*, yielded the following per-centage results :—

Lime	34·04 per cent.
Magnesia	1·86 „
Ammonia	1·12 „
Phosphoric acid . . .	43·35 „
Carbonic acid . . .	trace
Water, and a minute proportion of organic matter	19·54 „

From the relations which the small proportions of magnesia and ammonia, included in the above results, bear to each other, they evidently exist in the substance in the form of ordinary ammonio-phosphate of magnesia, $2MgO . NH_4O . PO_5 + 12$ Aq :— 1·86 per cent. of magnesia in this form would require 1·20 per cent. of ammonia; the per-centage obtained was 1·12. By calculating from the per-centage of magnesia, the proportion of the above double-salt existing in admixture with the phosphate of lime, the following numbers are obtained :—

Magnesia	1·86 per cent.
Ammonia	1·20 „
Phosphoric acid . .	3·35 „
Water	5·02 „

The amount of ammonio-phosphate of magnesia present in the specimen analysed would, therefore, be 11·43 per cent. Deducting the above numbers from the analytical results obtained, the following proportions of phosphoric acid, lime, and water remain :—

Lime	34·04
Phosphoric acid	40·00
Water	14·52

which, calculated upon one hundred parts, yield the following numbers :—

Lime	38·44
Phosphoric acid	45·17
Water	16·39
	100·00

The proportions which the acid and base bear to each other in these numbers, admit the conclusion that the form in which they are combined is in the proportion of two equivalents of lime to one of phosphoric acid, the lime being about three per cent. in excess of the amount required to form a salt containing two equivalents of the base, while it is more than twelve per cent. below what would be required to form a tri-phosphate.

I was at first disposed to regard this phosphate of lime, which, as above stated, frequently exists in the form of distinct crystals, as the crystallized di-phosphate, which may be produced by adding lime-water to the acid phosphate of lime, $CaO . 2HO . PO_5$, by dissolving lime in a slight excess of phosphoric acid, or by digesting the amorphous tri-phosphate of lime with a proportion of an acid, such as hydrochloric acid, insufficient for its solution. But the composition of this salt, which Bödeker describes as containing four equivalents of water of crystallization ($2 CaO . HO . PO_5 + 4$ Aq.) does not accord with the numbers obtained.* On comparing them, however, with the per-centage proportions required for a di-phosphate of lime of the formula $2 CaO . HO . PO_5 + 2$ Aq., containing, therefore, two equivalents less of water of crystallization than the salt described by Bödeker, they correspond pretty closely, particularly when it is remembered that a small proportion of the lime discovered in the deposit existed in the form of carbonate.

The following is a comparison of the per-centage results with the numbers demanded by the above formula, $2 CaO . HO . PO_5 + 2$ Aq.:—

2 CaO ..	56 ..	36·13 ..	38·44
PO_5 ..	72 ..	46·45 ..	45·17
3 HO ..	27 ..	17·42 ..	16·39
	155	100·00	

It is, however, also not improbable that the deposits of phosphate of lime which have been described, and which vary considerably in the degree of crystalline structure exhibited, may consist of variable mixtures of amorphous and crystallized di-phosphate of lime.

* In Gmelin's Handbook, vol. iii. p. 195, the theoretical numbers given for comparison with the results of Bödeker's analysis of this salt are calculated upon *four* instead of *five* equivalents of water; hence the results of that chemist do not appear to agree well with the formula given, whereas they accord closely with those demanded by the formula $2 CaO. HO. PO_5 + 4$ Aq.

XIX.—*On the Chemical Constitution and Artificial Formation of Taurine.*

By Hermann Kolbe, of Marburg.

Some years ago, Strecker* made the interesting observation that isethionate of ammonia, when heated to 210° C., gives off water, and is converted into taurine. By this discovery, as well as by the more recent observation of Gibbs,† that taurine treated with nitrous acid is reconverted into isethionic acid, the existence of intimate relations between taurine and isethionic acid was placed beyond doubt; but the question relating to the chemical constitution of taurine, with which that of isethionic acid is closely connected, still remained undecided. That taurine is not the amide of isethionic acid, is sufficiently shown by its behaviour with hydrate of potash, which does not eliminate ammonia from it till heated to the melting point, and then completely decomposes it.

I believe that I have found the key to the solution of this problem, by an experimental confirmation of the conjecture which I threw out a short time ago,‡ that taurine is related to isethionic acid in the same manner as alanine to lactic acid. In the same sense that the two last-mentioned bodies may be regarded as derivatives of ethyl-carbonic (propionic) acid, that is to say, alanine as amido-ethyl-carbonic acid, and lactic acid as oxy-ethyl-carbonic acid,—so likewise may taurine and isethionic acid be viewed as derivatives of ethyl-sulphuric acid, namely taurine as amido-ethyl-sulphuric acid, and isethionic acid as oxy-ethyl-sulphuric acid: these relations are exhibited by the following formulæ:

$HO.C_4H_5[C_2O_2]O$ Propionic acid.	$HO.C_4H_5[S_2O_4]O$ Ethyl-sulphuric acid.
$HO.C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}[C_2O_2]O$ Alanine.	$HO.C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}[S_2O_4]O$ Taurine.
$HO.C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}[C_2O_2]O$ Lactic acid.	$HO.C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}[S_2O_4]O$ Isethionic acid.

* Ann. Ch. Pharm. xci, 101.

† Jahresbericht der Chemie, xi, 550.

‡ Ann. Ch. Pharm. cxii, 241.

To the assumption that taurine and alanine are so nearly related to each other as these formulæ indicate, it may be objected that taurine does not possess the power which is common to glycocine, alanine, leucine, aspartic acid, amidobenzoic acid, and amido-acids in general, of forming saline compounds both with bases and with acids. But independently of the fact that the organic derivatives of sulphuric acid differ in many points from those of carbonic acid, the following consideration is of especial importance in connection with the present inquiry.

It must, in the first place, be presumed that, by the introduction of amidogen into the ethyl-molecule, the acid properties of ethyl-sulphuric acid will be weakened in the same degree as in alanine, the body derived in like manner from ethyl-carbonic (propionic) acid. But inasmuch as ethyl-sulphuric acid is a stronger acid than propionic acid, it is not surprising that even the weak basic properties of amidated propionic acid should be wanting in the amidated ethyl-sulphuric acid.* On the other hand, this latter acid might be expected to exhibit properties which have not hitherto been actually observed in taurine. Guided by these considerations, I have made several experiments with pure taurine prepared from ox-bile, the results of which I will here briefly communicate.

Taurine dissolved in fuming hydrochloric or strong nitric acid, crystallizes unaltered from the solution on evaporation; moreover, it does not increase in weight when exposed to an atmosphere of dry hydrochloric acid gas, either at ordinary temperatures or when heated. In order to determine whether taurine, like alanine, is capable of forming crystalline compounds with salts, I mixed the concentrated aqueous solutions of equivalent quantities of taurine and chloride of potassium, and abandoned the solution to spontaneous evaporation: pure taurine then crystallized out first, and afterwards chloride of potassium. Neither does the hydrochloric acid solution of taurine yield any compound with bichloride of platinum, alcohol added to the solution producing a precipitate of pure taurine.

It appears therefore that taurine does not exhibit the basic properties possessed by other amido-acids; but, on the other hand, it is by no means destitute of the power of uniting with

* Methyl-sulphuric acid, the analogue of acetic acid, does not yield marsh-gas when treated with soda-lime; neither does benzyl-sulphuric acid, the analogue of benzoic acid, yield benzole when thus treated. Other examples of these differences of character are afforded by the observations lately communicated by Vogt (Ann. Ch. Pharm. cxix, 143), and Keller (*ibid.* 153).

bases; and, although I have not succeeded in preparing salts of taurine in the solid form, the following experiments show that it is really capable of forming such compounds.

A saturated aqueous solution of taurine, in which absolute alcohol immediately produces a copious precipitate, is not precipitated, or even clouded, by a mixture of absolute alcohol and ammonia; but if the solution be then exposed to the air till the ammonia is volatilized, the taurine separates in beautiful crystals. Neither is a concentrated aqueous solution of taurine containing free potash, precipitated by absolute alcohol—a property which may be successfully applied to the separation of taurine from other compounds insoluble in alcohol. Carbonic acid, passed into the solution, separates the taurine in its original state.

Hydrated oxide of lead is taken up in considerable quantity by a hot aqueous solution of taurine, the clear filtered liquid becoming only slightly turbid on cooling. On exposure to the air, it deposits a considerable quantity of carbonate of lead. An aqueous solution of taurine does not decompose carbonate of lead, even at the boiling heat.

These results show that taurine is by no means an indifferent body, as it has hitherto been considered, but rather a weak acid, the acid properties of the primary compound, ethyl-sulphuric acid, being weakened in it by the substitution of amidogen for hydrogen, to nearly the same extent as, in trichloraniline, the basic properties of aniline are weakened by the introduction of chlorine.

The consideration of taurine as amido-ethyl-sulphuric acid, is further supported by its formation from isethionic acid by a process analogous to that of alanine from lactic acid.

Chloride of Chlorethyl-sulphuric Acid, and Chlorethyl-sulphuric Acid.

If isethionic acid be really constituted similarly to lactic acid, as above suggested, it may be expected to exhibit, under the influence of pentachloride of phosphorus, a transformation similar to that of lactic acid, yielding in fact the chloride of chlorethyl-sulphuric acid thus:—

Lactate of potash. Chloride of Chloro-propionic acid.

$$KO.C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}[C_2O_2]O + 2PCl_5 = C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}[C_2O_2]Cl + KCl + HCl + 2PO_2Cl_3.$$

Isethionate of potash. Chloride of Chlorethyl-sulphuric acid.

$$KO.C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}[S_2O_4]O + 2PCl_5 = C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}[S_2O_4]Cl + KCl + HCl + 2PO_2Cl_3.$$

It may further be expected that the chlorethyl-sulphuric acid, resulting from the action of water on this chloride, will be converted, by appropriate treatment with ammonia, into taurine, just as the analogously constituted compound, chloropropionic acid, is thereby converted into alanine:

$$HO.C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}[C_2O_2]O + 2H_3N = HO.C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}[C_2O_2]O + NH_4Cl.$$

Chloropropionic acid. Alanine.

$$HO.C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}[S_2O_4]O + 2H_3N = HO.C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}[S_2O_4]O + NH_4Cl.$$

Chlorethyl-sulphuric acid. Taurine.

These expectations have been completely fulfilled by the results of the following experiments:—

To prepare chloride of chlorethyl-sulphuric acid, 60 grammes (1 at.) of finely pulverized isethionate of potash, dried at 100° C., were introduced, together with 150 grms. (2 ats.) of pulverulent pentachloride of phosphorus, into a capacious tubulated retort, the two substances being mixed together as completely as possible with a bent glass rod. The mixture, after a while, begins to get warm and to liquefy, and at length boils, with copious evolution of hydrochloric acid fumes, a large quantity of oxychloride of phosphorus distilling over at the same time into the receiver. If, after this violent action is over, the retort be gently heated, nearly pure oxychloride of phosphorus distils over at first; afterwards, when the heat is raised, a much heavier, mobile, oily liquid, having a strong pungent odour, passes over in somewhat considerable quantity. This liquid consists mainly of the chloride of chlorethyl-sulphuric acid, while in the retort there ultimately remains a dry, blackish, saline mass.

The chloride of chlorethyl-sulphuric acid, which boils at about 200° C., may be easily and completely separated from the oxychloride of phosphorus by fractional distillation; nevertheless, I have not succeeded in preparing this compound quite pure, apparently because a quantity of chloride of isethionic acid $C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}[S_2O_4]Cl$, is formed at the same time, which

chloride boils at nearly the same temperature as the chloride of chlorethyl-sulphuric acid. A precisely similar observation was made by myself and Dr. Lautemann with regard to the distillation of salicylic acid, or salicylate of soda, with pentachloride of phosphorus, the chloride of salylic acid thereby produced being always more or less accompanied by chloride of salicylic acid.

The distillate which passes over in the rectification of the crude product at 200° C.—at which the boiling temperature remains to a certain degree stationary—is a nearly colourless, heavy liquid, which fumes in the air, does not mix with water, and has an intense and very persistent odour, strongly recalling that of volatile oil of mustard. Analysis gave the following numbers:

0·626 grm. burnt with oxide of copper gave 0·346 grm. carbonic acid and 0·150 grm. water, corresponding to 15·0 p. c. carbon and 2·6 p. c. hydrogen.

0·5055 grm. passed in the state of vapour over red-hot lime gave 0·7825 grm. chloride of silver = 38·3 p. c. chlorine.

0·604 grm. passed over red-hot carbonate of soda, which was finally heated in a stream of oxygen, yielded 0·905 grm. sulphate of baryta, corresponding to 20·8 p. c. sulphur.

The formula $C_4 \left\{ \begin{matrix} H_4 \\ Cl \end{matrix} \right\} [S_2O_4]Cl$ requires

	Calculated.		Found.
C_4	24	14·7	15·0
H_4	4	2·5	2·6
S_2	32	19·6	20·5
O_4	32	19·6	„
Cl_2	71	43·6	38·3
	163	100·0	

The somewhat too large amounts of carbon and sulphur shown by the analysis, on the one hand, and the great deficiency of chlorine on the other (a product obtained in another preparation yielded 39·2 p. c. chlorine), corroborate the supposition that the compound analysed contained a small quantity of chloride of isethionic acid.

Chloride of chlorethyl-sulphuric acid is but very slowly decomposed by water at ordinary temperatures. A drop of it covered with a large quantity of water did not disappear completely in

the course of a week. Heated with water to 100° C. in a hermetically sealed tube, it dissolves somewhat readily, yielding hydrochloric and chlorethyl-sulphuric acid, and losing its odour at the same time. It dissolves easily in potash, with great evolution of heat; also in aqueous ammonia, with abundant formation of sal-ammoniac. Taurine is not produced in this last reaction, but probably the amide of amido-ethyl-sulphuric acid.

The solution of chloride of chlorethyl-sulphuric acid in absolute alcohol, even after being heated in a hermetically sealed tube to 100° C., does not yield any chlorethyl-sulphate of ethyl on addition of water.

If the strongly acid solution obtained by heating the chloride of chlorethyl-sulphuric acid with water in sealed tubes for several days be completely freed from admixed hydrochloric acid, by evaporation, first over the open fire, afterwards over the water-bath, a thickish acid liquid is obtained, consisting chiefly of chlorethyl-sulphuric acid. This acid forms crystallizable salts with oxide of lead, oxide of silver, and other bases. For the preparation of the pure acid, I have used the silver-salt, which crystallizes easily and in beautiful forms.

The solution of the crude acid diluted with a moderate quantity of water dissolves carbonate of silver with effervescence. After it has been treated, for a while with a slight excess of the carbonate of silver, without heating, but with frequent agitation, the clear filtered saline solution, which is very sensitive to the action of light, and still more to that of heat, is evaporated nearly to dryness in vacuo over sulphuric acid, being at the same time protected from the light. The crystalline mass separated from the mother-liquor, and washed with a little cold water, is well comminuted and re-dissolved in the smallest possible quantity of cold water, and on again leaving the filtered solution to evaporate in vacuo, the pure chlorethyl-sulphate of silver crystallizes out in large transparent rhombic prisms, the mother-liquor yielding an additional quantity on further concentration. Analysis gave the following numbers:

1·256 grm. of the silver-salt burnt with oxide of copper yielded 0·440 grm. carbonic acid and 0·182 grm. water = 9·5 p. c. carbon and 1·6 p. c. hydrogen.

1·015 grm. ignited with carbonate of soda in a stream of

oxygen, yielded 0·987 grm. sulphate of baryta = 13·3 p. c. sulphur.

1·257 grm. precipitated with hydrochloric acid, yielded 0·703 chloride of silver = 43·1 p.c. silver.

The formula $AgO.C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right\} [S_2O_4]O$ requires

	Calculated.		Found.
C_4	24·0	9·5	9·5
H_4	4·0	1·6	1·6
Cl	35·5	14·1	—
S_2	32·0	12·7	13·3
O_6	48·0	19·1	—
Ag	108·0	43·0	43·1
	251·5	100·0	

The aqueous solution of this salt is rapidly decomposed by heat, especially at the boiling temperature, with separation of chloride of silver, isethionic acid being doubtless reproduced; but the decomposition is never complete, even after the heating has been continued for several days.

The aqueous solution of chlorethyl-sulphuric acid obtained by precipitating the silver-salt with sulphuretted hydrogen, has a strong acid reaction, and sustains a boiling heat without alteration. When concentrated by evaporation, finally in vacuo over oil of vitriol, it crystallizes in long colourless prisms, which are highly deliquescent, and melt at a moderate heat.

The salts of chlorethyl-sulphuric acid are easily, and to all appearance completely, decomposed by boiling with free alkali, yielding a metallic chloride and probably an isethionate. Carbonate of potash produces the same decomposition at the boiling heat.

Attempts to replace the chlorine of chlorethyl-sulphuric acid by hydrogen have, to a certain extent, given negative results. The free aqueous acid boiled with zinc, gives off a large quantity of hydrogen, without forming a trace of hydrochloric acid. Addition of sulphuric acid increases the evolution of gas, but even in this case the hydrogen does not remove any chlorine from the acid. Neither is any decomposition produced in the acid solution by the hydrogen evolved by a powerful voltaic current with two amal-

gamated zinc plates as the electrodes. The replacement of the chlorine by hydrogen is, however, easily effected by the electrolysis of a weak alkaline solution of an alkaline chlorethyl-sulphate, or by treating the soda-salt in the cold with sodium-amalgam.

In this respect, chlorethyl-sulphuric acid exhibits considerable resemblance to the homologous compound, chlormethyl-sulphuric acid, which I obtained in 1845 from trichlormethyl-sulphuric acid, and to which I then gave the name of chlorelayl-hyposulphuric acid.*

Taurine.

It has already been observed that chlorethyl-sulphuric acid is converted into taurine by the action of ammonia. The transformation is easily effected as follows: Dry chlorethyl-sulphate of silver is sealed up in a strong glass tube, with a large excess of the strongest aqueous ammonia,† and the clear saline solution which is immediately formed on agitation is heated to 100° C. for several hours. The liquid remains unclouded, but, if subsequently evaporated over the water-bath, deposits a considerable quantity of chloride of silver. The dry residue dissolves in water, with the exception of the chloride of silver; the solution still retains a very small quantity of silver, which is best removed by adding a drop of hydrochloric acid immediately after the residue is dissolved.

The clear, slightly acid filtrate is evaporated to a small bulk, and mixed with strong alcohol, which precipitates a considerable quantity of taurine. The crystalline precipitate thus formed always contains, besides taurine, a variable quantity of another substance, which, when the whole is recrystallized from water, mixes with the beautiful crystals of taurine, in small white, opaque, crystalline nodules; this substance also gives off ammonia when boiled with potash-ley. I think it probable that this compound is the amide of taurine, $C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right\} \left. \begin{matrix} S_2O_4 \\ H_2 \end{matrix} \right\} N$, mixed perhaps with the amide of isethionic acid $C_4 \left\{ \begin{matrix} H_4 \\ HO_2 \end{matrix} \right\} \left. \begin{matrix} S_2O_4 \\ H_2 \end{matrix} \right\} N$.

* Ann. Ch. Pharm. liv, 168, ff.

† With alcoholic ammonia, the product obtained is not taurine, but another crystalline compound, not yet investigated.

To remove this adventitious substance, the impure taurine precipitated by alcohol was boiled with potash-ley (in another preparation the same treatment was immediately applied to the crude solution of taurine filtered from the chloride of silver after addition of hydrochloric acid) till the odour of ammonia was no longer perceptible, and the highly concentrated alkaline solution was then mixed with about twenty times its volume of absolute alcohol, which, as already remarked, does not precipitate taurine from its alkaline solutions. The clear filtrate, diluted with water, evaporated, slightly acidulated with hydrochloric acid, and again evaporated to a small bulk, yields, on addition of a large quantity of strong alcohol, a copious crystalline precipitate of taurine, contaminated only with a small quantity of chloride of potassium. A better method of precipitating the taurine from its alkaline alcoholic solution might perhaps be to pass carbonic acid into it. By recrystallization from water, it is ultimately obtained in large hard crystals, and perfectly pure.

I have subsequently found that the crude chlorethyl-sulphuric acid obtained by treating the chloride of chlorethyl-sulphuric acid with water, may be used, instead of the silver-salt, for the preparation of taurine. The liquid, after being freed by evaporation from admixed hydrochloric acid, is to be neutralized with ammonia, and the ammonia-salt evaporated to dryness, and heated for some time to 100° C., in a hermetically sealed tube, with excess of saturated aqueous ammonia. The resulting solution is then to be treated in the manner above described, excepting that the larger quantity of sal-ammoniac which it contains must be removed by boiling with hydrated oxide of lead.

Taurine prepared by either of these processes agrees in every respect with that which is obtained from ox-bile, as I have convinced myself by comparative experiments. Analysis gave the following numbers:

0·3855 grm. taurine burnt with oxide of copper in a tube containing chromate of lead and metallic copper at its open end, finally in a stream of oxygen, gave 0·2715 grm. carbonic acid and 0·199 water = 19·3 p. c. carbon and 5·7 p. c. hydrogen.

0·3955 grm. ignited with carbonate of soda in a stream of oxygen, yielded 0·743 grm. sulphate of baryta = 25·8 p. c. of sulphur.

The formula $HO.C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right\} [S_2O_4]O$ requires

	Calculated.		Found.
C_4	24	19·2	19·3
H_7	7	5·6	5·7
N	14	11·2	—
S_2	32	25·6	25·8
O_6	48	38·4	—
	125	100·0	

Glycocine, $C_4H_5NO_4$, and taurine, $C_4H_7NS_2O_6$, which exist in bile, together with cholalic acid—doubtless in the same state of combination as glycocine and benzoic acid in the hippuric acid of urine—appear like heterogeneous compounds, when regarded merely according to their empirical formulæ; nevertheless, they are nearly related to one another, as shown by the simple mode of formation of taurine just described.

If glycocine be regarded as amido-acetic acid, that is, as carbonic acid in which one of the extra-radical oxygen-atoms is replaced by amido-methyl, then taurine must be regarded as an analogous derivative of sulphuric acid, excepting that one of the extra-radical oxygen-atoms is replaced by amido-ethyl instead of by amido-methyl, as shown by the following formulæ:

$HO.C_2 \left\{ \begin{matrix} H_2 \\ H_2N \end{matrix} \right\} [C_2O_2]O$ Glycocine.

$HO.C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right\} [S_2O_4]O.$ Taurine.

Since it is known that, besides glycocine, many similarly constituted homologous derivatives of the fatty acids—especially leucine (amido-propionic acid)—are widely diffused in the animal body, the observation that the functions of taurine in the bile-compounds, is precisely similar to that of glycocine, lends some degree of probability to the supposition that the animal body contains, besides taurine, other similarly constituted homologous derivatives of sulphuric acid, especially amido-methyl-sulphuric acid, the direct analogue of glycocine, and amido-amyl-sulphuric acid, analogous to leucine, both of which compounds perhaps enter into the composition of many animal substances rich in sulphur, such as horn, hair, &c.

$HO.C_2\left\{\begin{matrix}H_2\\H_2N\end{matrix}\right\}[C_2O_2]O$
Amido-methyl-carbonic acid. (Glycocine).

$HO.C_2\left\{\begin{matrix}H_2\\H_2N\end{matrix}\right\}[S_2O_4]O$
Amido-methyl-sulphuric acid.

$HO.C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}[C_2O_2]O$
Amido-ethyl-carbonic acid. (Alanine).

$HO.C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}[S_2O_4]O$
Amido-ethyl-sulphuric acid. (Taurine).

$HO.C_{10}\left\{\begin{matrix}H_{10}\\H_2N\end{matrix}\right\}[C_2O_2]O$
Amido-amyl-carbonic acid. (Leucine).

$HO.C_{10}\left\{\begin{matrix}H_{10}\\H_2N\end{matrix}\right\}[S_2O_4]O$
Amido-amyl-sulphuric acid.

I regard it as by no means a thankless problem to search for these and other compounds homologous and analogous to taurine in the animal body, and especially in the secretions which are peculiarly rich in sulphur. From the above-described mode of formation of taurine, we might also expect that the artificial preparation of these other compounds would not be difficult. I am at present engaged with the attempt to convert chlormethyl-sulphuric acid—a compound very closely resembling chlorethyl-sulphuric acid—by the action of ammonia, into amido-methyl-sulphuric acid, an acid which may be expected to exhibit considerable resemblance to taurine.

XX.—*On the Determination of Alkalies in Fire-clays and Fire-bricks.*

By G. GORE.

As the process of bringing pulverized fire-clay, or fire-brick, into solution by digestion with aqueous (or treatment with gaseous) hydrofluoric acid, for the determination of the alkalies contained in it, is very tedious,—and as the other process employed for the same purpose, viz., mixing the substance with nitrate of baryta, and subjecting it to an intense white heat, does not produce a perfectly fused and fluid mixture, but only agglutinates the materials into a semi-fused mass,—I have adopted the following method, which has proved in my experience more effectual and satisfactory.

Three parts of perfectly dry nitrate of baryta, very finely pulverized, to prevent decrepitation, were mixed with three parts of equally dry and finely powdered fluoride of barium, and one part of the finely pulverized clay or brick. The mixture was projected, in successive portions, into a red-hot platinum crucible, a little of the nitrate and fluoride, unmixed with the clay, being reserved and spread upon the top, and the mixture then heated as highly as possible over a Bunsen's burner. The crucible was then transferred to a Griffin's analytical gas furnace, and heated during fifteen minutes to a still higher degree, then removed and cooled.

Any particles of the mixture which now adhered to the edge of the crucible were scrupulously removed and added to the general contents. The crucible was placed in a Griffin's gas blast furnace, and covered with a stout sheet of platinum, and heated to the maximum power of that furnace during twenty minutes; the lid was then removed; the contents of the crucible (which were perfectly liquid) were poured into a shallow, massive vessel of cast-iron, and a cold block of cast-iron at once placed upon the heated mass. It quickly decrepitated into numerous small pieces, which were collected, and carefully crushed still smaller in a steel crushing mortar; and the resulting coarse powder, together with the crucible, and any portions adhering to it, was placed in a platinum dish, and covered with pure sulphuric acid. A very moderate heat was now applied, the decomposition proceeded rapidly, and the resulting sulphate of baryta floated upon the acid as a bulky scum; as soon as the action declined, further heat was applied, and the contents of the vessel were evaporated to perfect dryness, to remove excess of sulphuric acid; the residue was now digested with abundance of hot water, and the liquid part, containing the whole of the alkalies in solution, was then treated in the usual manner. The portion of the process here described occupied about four hours.

The results obtained in three different analyses agreed very closely with each other and with three analyses of the same substance made with aqueous hydrofluoric acid.

XXI.—*Note on Professor Bolley's Communication "On some Physical Properties of the Alloys of Tin and Lead."*

By A. Matthiessen, F.R.S.

In the last number of the "Journal of the Chemical Society" (vol. xv., p. 30), Professor Bolley gives an account of Mr. Pillichody's research into some physical properties of the alloys of tin and lead.

A table is there given purporting to be a comparison of the values found by Kupffer, Long, Thomson, and Pillichody, for the specific gravities of these alloys. Long's determinations, here quoted, having been made at my request and recorded in my paper, "On the Specific Gravity of Alloys,"* I feel bound to point out a mistake into which Professor Bolley has fallen with regard to what he calls the *calculated specific gravities* in the table referred to. These are, he says, "calculated from the quantities and specific gravities of the component metals;" whereas it is sufficiently obvious, and I have already drawn attention to the point in my paper, quoted above, that they ought to be calculated, not from the *quantities* (or weights) but from the *volumes* of the component metals; for, when no expansion or contraction takes place, the specific gravities of the components take part in the specific gravity of the compound in the ratio of their relative volumes, and not in the ratio of their weights.

Hence the great apparent differences between the specific gravities of the alloys of tin and lead as found by Long, and the calculated values given in Bolley's table, the latter being, as I have said, calculated according to a wrong method. By reference to my paper in the "Philosophical Transactions," it will be seen that the experimental specific gravities found by Long agree even more closely with the numbers calculated according to the right method than do those of Kupffer, whereas the contrary appears from this table. The reason of this is, that the calculated specific gravities, with which Kupffer's results are here compared, are those given by himself, and are rightly calculated.

To show clearly the incorrectness of the method of calculating the specific gravities by which those in the table were calculated,

* Phil. Trans. 1860, p. 177.

let us see what the theoretical specific gravity will be of an alloy composed of 1 grm. aluminum and 1 grm. platinum, of course under the supposition that no contraction or expansion takes place. Then, according to the method employed in Professor Bolley's table, the specific gravity will be equal to $\frac{1 \times 2{\cdot}5 + 1 \times 21{\cdot}45}{1 + 1} = 11{\cdot}97$, taking the specific gravity of aluminum equal to 2·5, and that of platinum equal to 21·45, whereas the theoretical specific gravity of the alloy is only 4·46 : for if we assume that no contraction or expansion takes place when the two metals alloy with each other, then we may look on such an alloy, when taking its specific gravity, as if the two metals were hanging side by side in the water. Now, 1 grm. of aluminum will displace 0·4 grm. water, and 1 grm. platinum 0·047 grm. If, therefore, the theoretical specific gravity of the alloy be required, it will be the weight of the two metals divided by the quantity of water displaced by them, $o_r \frac{2}{0{\cdot}4 + 0{\cdot}047} = 4{\cdot}46$.

It further appears, that, when the correction I have indicated is introduced, Mr. Pillichody's experiments confirm those of Long, as to the greatest expansion taking place in the formation of the alloy $Sn\,Pb_2$, and not of the alloy Sn Pb, as stated, by Professor Bolley.

XXII.—*Observations on Silica.*

By Arthur H. Church, B.A.

The recent researches of Mr. Graham in dialysis have shown us how to prepare a pure aqueous solution of silica of considerable strength and with great ease. Pure water, according to Kirwan, is capable of taking up no more than one-thousandth part of its weight of hydrate of silica freshly precipitated, while there is no difficulty in obtaining, by the dialytic method, a liquid containing fourteen per cent. of that substance. The other processes for procuring silica in solution are less satisfactory, for it is difficult to free the product from hydrosulphuric acid when sulphide of silicon is used; and on heating gelatinous silica with water in a glass tube under pressure, the glass is acted on, and a portion of alkaline silicate formed,

A solution of silica containing more than 0·5 per cent. of the anhydride cannot be kept long without change; but I have observed no alteration as to transparency or fluidity in a solution containing 0·47 per cent. after the lapse of three months. With respect to stronger solutions, the process of gelatinization is generally more or less gradual. Freshly prepared, a solution containing 3 per cent. of anhydrous silica was perfectly limpid, and nearly as mobile as water; after the lapse of six days, it acquired the consistence of glycerin, and then rapidly became ropy, the silica separating in gelatinous masses. The solution in this case was kept in a well-stoppered bottle. Solutions of silica obtained by dialysing an alkaline silicate after addition of hydrochloric acid, seem, according to my experiments, to retain their fluidity longer than those of the same strength where sulphuric acid has been used; and as a general rule, the purer the solution and the freer from acids and salts, the longer may it be preserved without change.

The chlorides of barium, strontium, and calcium, and many other salts, produce no immediate precipitate in an aqueous solution of silica; but solutions of the alkaline earths at once throw down the whole of the dissolved substance; or, if they be added in insufficient quantity, the silicate formed causes the remainder of the silica to separate as a jelly. This action is still more prompt if the carbonates of calcium, strontium, or barium be made to react upon the silica solution. One milligramme of pure carbonate of calcium in fine powder was put at the bottom of a beaker, and then 100 cubic centimetres of a 1 per cent. silica solution were poured upon it: in ten minutes, the mixture was a firm jelly, and the vessel could be inverted without the loss of any of its contents.

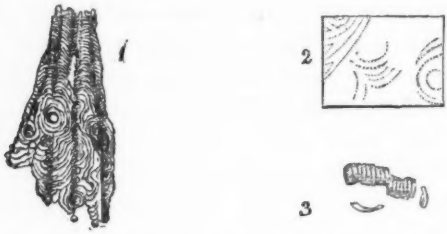
I cannot but think that this singular deportment of the aqueous solution of silica with the carbonates of the alkaline earths tends to throw great light upon several important geological and mineralogical questions. Silica, we know, is almost an invariable constituent of the waters of the earth, and in several cases it exists in solution in considerable quantity, rather as silicic acid than as an alkaline silicate. Several springs in Iceland, at Luzon in the Philippine Islands, and in New Zealand, deposit a beautiful quartz-sinter, containing scarcely more sodium and potassium than common flint. But the action of far weaker solutions of silica may, I believe, be traced very frequently in less striking but more common conditions. I have endeavoured to

test this supposition by a series of experiments, an example of which I will now describe.

A curious silicified substance, at once a mineral and a fossil, occurs in the triassic red conglomerate of Torbay and its neighbourhood; similar, if not identical, bodies are found in other parts of Great Britain, and also in a few foreign localities. This mineralized fossil, to which the name of "Beekite" has been assigned, presents itself under such a variety of aspects as to baffle description, so far as regards its physical features; its chemical composition is more constant. Originally corals or shells, and therefore consisting in great measure of carbonate of calcium, beekites have become so modified in constitution as to contain on an average no less than 92 per cent. of silica; a small but variable amount of calcium occurs in them, but this exists as silicate rather than carbonate; a few exceptional cases have been noted, where the process of silicification has been arrested before completion, and where the interior of the beekite may be completely dissolved away by hydrochloric acid, though the outside is not affected by this reagent. I have attempted to transform corals and shells into a substance resembling that of which beekites consist. The trial was made in this wise. A fragment of recent coral was fitted tightly into the neck of a funnel, and a solution of silica in water containing dissolved air and carbonic acid was allowed to fall upon it drop by drop. The liquid which filtered through contained much carbonate of calcium, but no silica, while the coral ultimately retained very little carbonate of calcium. The silica-solution should be very dilute, about 0·15 per cent., otherwise part of the silica will gelatinize on the surface of the coral and prevent further action.

I have endeavoured also to illustrate, by means of the aqueous solution of silica, that tendency to deposition, in a circular or globular form, which is so marked a characteristic of many siliceous minerals, such as quartz-sinter, eyed agate, bubble-chalcedony, and especially beekite. In the latter case, the surface of the specimen generally shows a number of tubercles surrounded by systems of concentric ridges. So strongly is this circular tendency developed in some instances, that a fragment of a silicified pecten, in my possession, shows a system of rings, partly situated in a furrow of the outer aspect of the shell, then bent upwards to follow the natural curve of a ridge, and then turned down into

another furrow. (The inner and more level aspect of this fragment is shown in Fig. 1.) I was anxious to see whether such



circular forms could be attained artificially, and the more so as Mr. Rainey has obtained similar globular crystals of carbonate of calcium. Although I have not at present arrived at any definite conclusion on the subject, I have yet observed, in working with an aqueous solution of silica, several phenomena which may suggest an answer to the question. Among these phenomena the following may be mentioned: the irregular spherical masses into which a solution of silica often dries up in the air, the faint curved markings developed in a piece of oyster-shell after artificial silicification (see Fig. 2), and the singular narrow flakes into which the film of silica, forming round and just above the margin of its aqueous solution, when evaporating in a dish or beaker, divides. These narrow strips curl inwards, the ends meet, and the rings or sections of cylinders thus formed accumulate in the liquid, presenting an appearance of great interest, the origin of which was not at first sight apparent (see Fig. 3).

XXIII.—*On Isoprene and Caoutchin.*

By C. GREVILLE WILLIAMS.

[Abstracted from the "Philosophical Transactions," 1860, p. 241.]

THE products of the destructive distillation of caoutchouc have been studied by several chemists. The results hitherto obtained

are, however, quite irreconcilable. Gregory* appears to have been the first to direct attention to them, but it is evident that even at the time of writing his "Handbook of Organic Chemistry" he was far from considering the true nature of the products as having been ascertained; for, at p. 346, he says: "When exposed to heat, caoutchouc first melts and then distils, yielding a mixture of several oily liquids, all of which, as well as pure caoutchouc itself, are carbo-hydrogens. Some of these oils boil at 90°, others at 680° Fahr.; and at intermediate points I found that one highly rectified oil which boiled at 96°, and had the composition of olefiant gas, yielded when acted on by sulphuric acid, an oil which boiled at 428°, and had the same composition. But most of these oils have the composition of oil of turpentine, C_5H_4, or $C_{10}H_8$. One of them, called *caoutchin*, gives with chlorine an oil, $C_{10}H_8+Cl$." Now the above statement contains undoubtedly the best account that could be given in so short a space of the results that had been obtained up to the time of publication of the work alluded to; but the account is somewhat confused, because the various observers all differ immensely in their results. The expressions C_5H_4 and $C_{10}H_8$, as used by Gregory, merely indicate arithmetical relations, and are not to be received as definite formulæ; for, in the first place, C_5H_4 is, according to our present views, an impossible formula†, and in the next, caoutchin is $C_{20}H_{16}$, not $C_{10}H_8$. No chemist up to the present time has proved a hydrocarbon of the formula $C_{10}H_8$ (= 4 volumes of vapour) to exist among the products of the distillation of caoutchouc. Such a formula, if proved, would be interesting, because, turpentine being the starting-point for Kopp's empirical formula for boiling-points, any substance having exactly half the number of atoms of carbon and hydrogen, with the same vapour-volume, would serve as the point of departure of numerous speculations upon boiling-points generally. The results of M. Bouchardat‡ are curious, and not easy to understand. He obtains olefiants and eupione, but no bodies of the formula n (C_5H_4), while Himly§ obtains bodies of the latter formula and no olefiants. The annexed table contains the results of the three chemists alluded to.

* Ann. Ch. Pharm. xvi., 61.
† C=6, H=1, O=8.
‡ Ann. Ch. Pharm. xxvii., 30.
§ Ibid. p. 40.

Name of observer.	Fluid found.	Boiling-point.	Density.	
			Liquid.	Vapour.
Gregory	C_nH_n	36° C.	0·654	
Bouchardat	C_2H_3	below 0	0·630 at 4°	
Bouchardat	Caoutchène (C_nH_n)	14·5	0·650	
Bouchardat	Eupione (?)	51	0·690 at 15°	
Himly	C_5H_4 (?)	30–40		
Himly	Caoutchin ($C_{20}H_{16}$)	171	0·842	4·461
Bouchardat	Hévéène (C_nH_n)	above 315	0·921 at 21°	

Results so contradictory would almost lead one to suppose that caoutchouc, like castor-oil, yielded different products according to the temperature; but in that case, the distillate obtained in a carefully conducted experiment should contain bodies belonging to the olefiants and the terebenes; this, however, is not the case. The weight of evidence appearing to prove olefiants to be the principal products, I had some hopes that caoutchouc, if carefully distilled, would yield hydrocarbons from which I might obtain certain at present unknown hydriodic ethers and their derivatives, in accordance with reactions first imagined by M. Berthelot, thus:—

$$\underbrace{C_nH_n + HI}_{\text{Olefiant plus hydriodic acid.}} = \underbrace{(C_nH_{n+1}) + I}_{\text{Iodide of alcohol-radical.}}$$

but I soon found that caoutchouc, when carefully distilled in iron vessels, yielded no olefiant whatever. This is, moreover, in perfect accordance with experiments made by me some years ago,* in which I showed that caoutchouc, like many other oils, decolorized the same quantity of bromine as oil of turpentine. A repetition of this experiment, made with great precaution to ensure success, will be found further on.

The distillation was conducted with care in an iron alembic, the lowest temperature being used consistent with the distillation of oils. In fact I even stopped the distillation before the whole of the last oil, hévéène, came over, in order to ensure the decomposition taking place in the simplest manner. The crude distillate

* "On a Process for estimating the Equivalents of some Fluid Hydrocarbons by means of Bromine," Chemical Gazette, 1853.

was very fœtid, and contained traces of volatile bases derived from the decomposition of a minute trace of vegetable caseine in the caoutchouc. The bases were removed by agitation of the oil with dilute sulphuric acid; the latter was then got rid of by washing with water, which, in its turn, was subsequently removed by digestion with sticks of potash. The fluid thus prepared was easily separated by fractional distillation into two portions, one boiling between 37° and 44° C., and the other between 170° and 180°. The fractional separation of the hydrocarbons in the crude distillate affords a very instructive example of the extraordinary extent to which boiling-points are lowered by successive rectifications. In the first rectification the product was very small, below 116° C. The greater part distilled between 116° and 193°. Only one-half came over below 204°. In the second rectification, a large fraction was obtained between 40° and 50°, then scarcely any distilled until between 170° and 180°, which latter fraction was very large. At 171°, the thermometer was often perfectly steady while an ounce distilled over, the entire contents of the retort not being much more than one and a half ounce. The lower fraction oscillated between 36° and 44°, the variability in its boiling-point being principally due to the presence of oxygen; for, by careful and repeated rectifications over sodium, it may be made to distil almost entirely between 37° and 38°. This fluid lies at the boundary line between gases and liquids; it is scarcely possible to wet the hand with it; and if poured from a moderate height in small drops, it is volatilized before reaching the floor. A very good way of observing the influence of small pressures upon its physical condition, consists in passing a few drops into a mercurial eudiometer standing vertically. The warmth of the hand applied to the top of the instrument is sufficient to convert it into vapour; but if the position of the eudiometer be then altered so as to stand almost horizontally, the increase of pressure is sufficient to condense the gas into a liquid, and, on the other hand, it is instantly vaporized again on restoring the eudiometer to its original position.

This hydrocarbon possesses a property which, even more than its extreme volatility, renders it troublesome to the analyst. Unlike very volatile fluids in general, it lines with a slight film of carbon the bulbs in which it is contained during combustion. It is true that the amount thus left is very small, but it is sufficient to render an exact determination of the carbon difficult. It being

of course necessary to have all the apparatus, oxide of copper, &c., as cold as possible, it was also not easy to keep the hydrogen as low as could be desired. The substance used in the first three analyses boiled between 37° and 38°, and was prepared from caoutchouc. The fourth and fifth analyses were made on a product from gutta percha. No. IV. boiled between 42° and 43°, and No. V. between 43° and 44°.

	Experiment.					Mean.	Calculation.		
	I.	II.	III.	IV.	V.				
Carbon .	88·3	87·8	87·9	87·8	88·1	88·0	C_{10}	60	88·2
Hydrogen	12·0	12·0	12·1	12·2	12·3	12·1	H_8	8	11·8
								68	100·0

leading to the empirical relation

$$n\ (C_5H_4).$$

Although the boiling-point indicated the value of n to be not greater than 2, it is plain that the liquid might possibly have a higher formula. The atomic weight was therefore determined from the density of the vapour, assuming it to possess the usual condensation to four volumes.

Mean of experiments.	Theory, $C_{10}H_8 = 4$ volumes.
2·44	2·3493

I have given the substance thus examined the name of *isoprene*.

The specific gravity of the liquid at 20° C. was found to be 0·6823.

It will be seen that none of the hydrocarbons examined by Gregory, Himly, or M. Bouchardat can be identified with that just described; and although the formulæ C_5H_4 and $C_{10}H_8$ have often been vaguely applied to the numerous isomers of turpentine, yet none of the hydrocarbons obtained by the above chemists have been shown to contain $C_{10}H_8$ *for four volumes of vapour*. The hydrocarbon discovered by Couerbe* in the fluid obtained by the powerful compression of resin gas, although of the same composition, differs too much in density (0·709) and boiling-point (50°) to be considered as identical.

* Ann. Ch. Phys. lxix., 184. J. pr. Ch. xviii., 165. Gmelin's Handbook, x., 411, Cavendish Society's Translation.

Action of Atmospheric Oxygen on Isoprene.

If isoprene be left in a partly filled bottle for some months, it gradually loses its fluidity, and at last even becomes quite viscid; at the same time it is found to have acquired powerful bleaching properties. It readily decolorizes sulphate of indigo, and, under certain circumstances, converts sulphide of lead into sulphate. It is, in fact, ozonized.

Schönbein was the first to show that oil of turpentine absorbed ozone when kept for a long time; and I subsequently observed several cases where ozone was capable of existing in contact with organic and inorganic matters without exerting any material action on them so long as the temperature was kept down. In these instances, immediately the heat rose beyond a certain point, the substance in contact with the ozone underwent oxidation. Thus, if a slip of lead test-paper be exposed to the vapours of sulphide of hydrogen until the paper has acquired a deep brown colour, and a drop of an ozonized oil be placed on it, no change ensues at ordinary temperatures; but if the paper moistened with the oil be warmed until the latter begins to volatilize, the sulphide is immediately oxidized and bleached.

But the most remarkable phenomenon perhaps yet known in connection with the ozonization of essential oils, takes place on submitting ozonized isoprene to distillation. If the temperature be kept as low as is compatible with the volatilization of the unaltered portion of the oil, a colourless limpid fluid distils over, having the composition and boiling-point of pure isoprene. As the operation proceeds, the fluid thickens, causing the temperature to rise somewhat suddenly. The ozone at this point instantly begins to act with energy, a cloudy vapour rises, accompanied by an intensely sharp odour, and the contents of the retort instantly solidify to a pure white, spongy, elastic mass, having, when successfully prepared, but slight tendency to adhere to the fingers. When pure, it is opaque; but if allowed to become exposed to the air, especially when warm, it becomes transparent, first on the edges, and subsequently throughout the whole mass. When burnt, it exhales the peculiar odour hitherto considered characteristic of caoutchouc itself. It is not easy to prepare or to preserve this substance of definite composition. If the heat be allowed to rise too rapidly during its formation, it becomes decomposed; and

if not heated sufficiently, a portion of the original hydrocarbon obstinately adheres, in spite of its extreme volatility when separate. However prepared, its composition is that of isoprene plus oxygen. If sufficient care be taken, the oxidation is perfectly definite. A specimen prepared with every precaution, and immediately analysed, afforded, on combustion with oxide of copper and oxygen gas, numbers agreeing with the formula $C_{10}H_8O$.

As regards the true formula of this substance, there is reason to suppose that the expression $C_{10}H_8O$ does not correspond to four volumes of vapour; but as it is not volatile without decomposition, and as its properties forbid any hope of its yielding compounds from which the true equivalent might be deduced, I am at present compelled to rest satisfied with obtaining the simplest arithmetical relation between the elements.

The above-described substance is, it is believed, unique in its characters, whether we regard its composition as the directly formed oxide of a hydrocarbon, or the mode of its production by the influence of ozone.

Caoutchin.

The formula $C_{20}H_{16}$ derived by M. Himly from his experiments upon the oil boiling between 171° and 173° is perfectly correct. My analyses confirm his results as regards both the per-centage composition and the vapour-density; the latter is, by my experiments, 4·647; by Himly's, 4·461; by calculation (4 vol.), it is 4·6986.

On the Relation between the first and second Hydrocarbons produced by distillation of Caoutchouc.

We are now, for the first time, in a position to understand the true connection between the two hydrocarbons which have been described. The relation between them is the same as that between amylene and paramylene, and, as in the case of those bodies, the second is twice as heavy in the state of vapour as the first.

The boiling-point of the bodies show very strongly the limited power of empirical formulæ, even when (like those of Kopp and Gerhardt) founded on the accurate observation of a vast number of bodies. Thus, amylene $C_{20}H_{20}$, containing four atoms of hydrogen more than caoutchin, should boil, according to Gerhardt's law, $15 \times 2 = 30°$ lower than that body, whereas the boiling point is only 11° lower. Again, amylene, containing two

atoms of hydrogen more than isoprene, should boil 15° lower, whereas it boils 2° higher.

The reduplication of a formula has not the same *relative* influence upon the boiling-point of amylene that it has upon that of isoprene; thus—

Paramylene, $C_{20}H_{20}$, boils at	160°	Caoutchin, $C_{20}H_{16}$, boils at	171°
Amylene, $C_{10}H_{10}$, boils at	39°	Isoprene, $C_{10}H_8$, boils at	37°
Difference . . .	121	Difference . .	134

Oil of turpentine boils at 160°, and is taken as the pivot round which the boiling-points of hydrocarbons should arrange themselves at distances proportioned to the number of atoms of carbon and hydrogen in their formulæ; yet caoutchin, which not only has the same formula, but gives almost identical reactions, boils at 171°, eleven degrees higher, and very near that of carvene, which is 173°.

Comparative experiments on the Action of Bromine on Caoutchin and Oil of Turpentine.

M. Himly had observed that chlorine and bromine act upon caoutchin, and that the products when distilled over a base, afforded an oil containing less hydrogen than caoutchin. He did not examine the nature of the reaction more closely.

I mentioned, at the commencement of this paper, that I had several years ago made an experiment on the mutual action of bromine and caoutchin, which led me to believe the latter to belong, not to the olefiants, but to the vast group of hydrocarbons isomeric with oil of turpentine. But that experiment having been made with the bromine and hydrocarbon undiluted, and, moreover, the caoutchin not having been prepared by myself, I considered it necessary to repeat it with several precautions not then observed.

The action of bromine upon the terebenes is peculiar, one atom, or four-volume equivalent, always requiring exactly four atoms of bromine to produce a colourless fluid. If the hydrocarbon and the bromine be diluted, the former with alcohol, the latter with water, the experiment may be made with considerable precision. For the purpose of comparing the isomers, I prepared some freshly dried and rectified turpentine and caoutchin. They were diluted

with sufficient alcohol for each of the resulting liquids to contain exactly ten per cent. of hydrocarbon. The bromine employed was in the state of a weak solution in water, twenty cubic centimetres containing 0·2527 of bromine. A small flask containing twenty cubic centimetres with the stopper in its place, was employed each time to measure the bromine-water, which was transferred to a large stoppered flask, every precaution being taken to prevent loss. The diluted hydrocarbon was then gradually dropped into the bromine-water from a Schüster's alkalimeter containing a weighed quantity. Considerable agitation was applied after each addition. When the bromine-water was nearly decolorized, the liquid was added very cautiously, and an interval of about half a minute allowed to elapse between each addition. When the fluid had become perfectly colourless, the alkalimeter was reweighed. The following numbers were obtained in eight experiments made in the manner described :—

Mean of turpentine experiments.	Mean of caoutchin experiments.
0·1074	0·1091

The identity of behaviour of caoutchin and oil of turpentine becomes very evident from the above experiments. The mean of the caoutchin results is nevertheless somewhat higher than that of the turpentine series; I ascribe this to caoutchin being, to a very slight degree, more sluggish in its action than oil of turpentine.

Action of Bromine on Isoprene.

I was exceedingly desirous of making experiments with weighed quantities of isoprene and bromine, in order to compare it with caoutchin. With this intent I made a solution of it in alcohol, the strength being the same as the turpentine and caoutchin solutions. But it was impossible to obtain the wished-for results, owing to the manner in which the isoprene volatilized from the solution while pouring it into the bromine-water.

Isoprene combines explosively with bromine, even in presence of seventy or eighty times its volume of water. When the vessel containing the bromine at the bottom and the isoprene on the surface is shaken, union takes place with a loud noise and considerable evolution of heat. A fine mobile bromine-compound is the result. When cohobated with excess of hydrate of potash, the

greater portion is entirely decomposed, yielding a black mass, the distillate having the same odour as that evolved under similar circumstances by the higher olefiants, but accompanied by a substance so irritating to the eyes as to render it very distressing to manipulate. On placing about one ounce in a flask, and adding a fragment of hydrate of potash to neutralize it, an explosion took place, the fluid being thrown in my face, and causing the most intense pain in the eyes. For several days no person could enter the laboratory without incurring great pain, accompanied by profuse lachrymation. The substance having in this unfortunate manner been lost, I am compelled to defer a more minute investigation of it.

Conversion of Caoutchin into Cymole and Paracymole.

In Gerhardt's classification of organic bodies, oil of turpentine is made to belong to the cymenic series; and it is even stated that Deville, by passing turpentine and carbonic acid through a tube heated to dull redness, obtained an oil which appeared to contain $C_{20}H_{14}$; carbonic oxide, water, and empyreumatic products being formed simultaneously. Disregarding the empyreumatic bodies, the following equation may be considered to explain the nature of the reaction:—

$$\underbrace{C_{20}H_{16}}_{\text{4 vols. oil of turpentine.}} + \underbrace{C_2O_4}_{\text{4 vols. carbonic acid.}} = \underbrace{C_{20}H_{14}}_{\text{4 vols. cymole.}} + \underbrace{2HO}_{\text{4 vols. water.}} + \underbrace{2CO}_{\text{4 vols. carbonic oxide.}}$$

Some experiments made by me a considerable time ago with oil of turpentine, led me to conceive the idea of converting it into cymole, or an isomer, by the alternate action of bromine and a highly electro-positive metal, and the identity in certain cases of the reactions of oil of turpentine and caoutchin rendered it probable that a similar product would be yielded with the latter. Experiment has completely confirmed this supposition.

If to a quantity of bromine and water in a stoppered flask caoutchin be gradually added, and the flask be shaken after each addition, a sharp hissing sound is heard, and combination takes place with great energy and considerable rise of temperature; at the same time a heavy oil, red at first but finally colourless, sinks to the bottom. The product when cold is as viscid as treacle. Its characters do not offer any great guarantee for purity; and the production of hydrobromic acid at the same time indicates

that while one portion of the halogen combines with the caoutchin, another seizes the most easily removable of its atoms of hydrogen, and yields the acid which is found dissolved in the water.

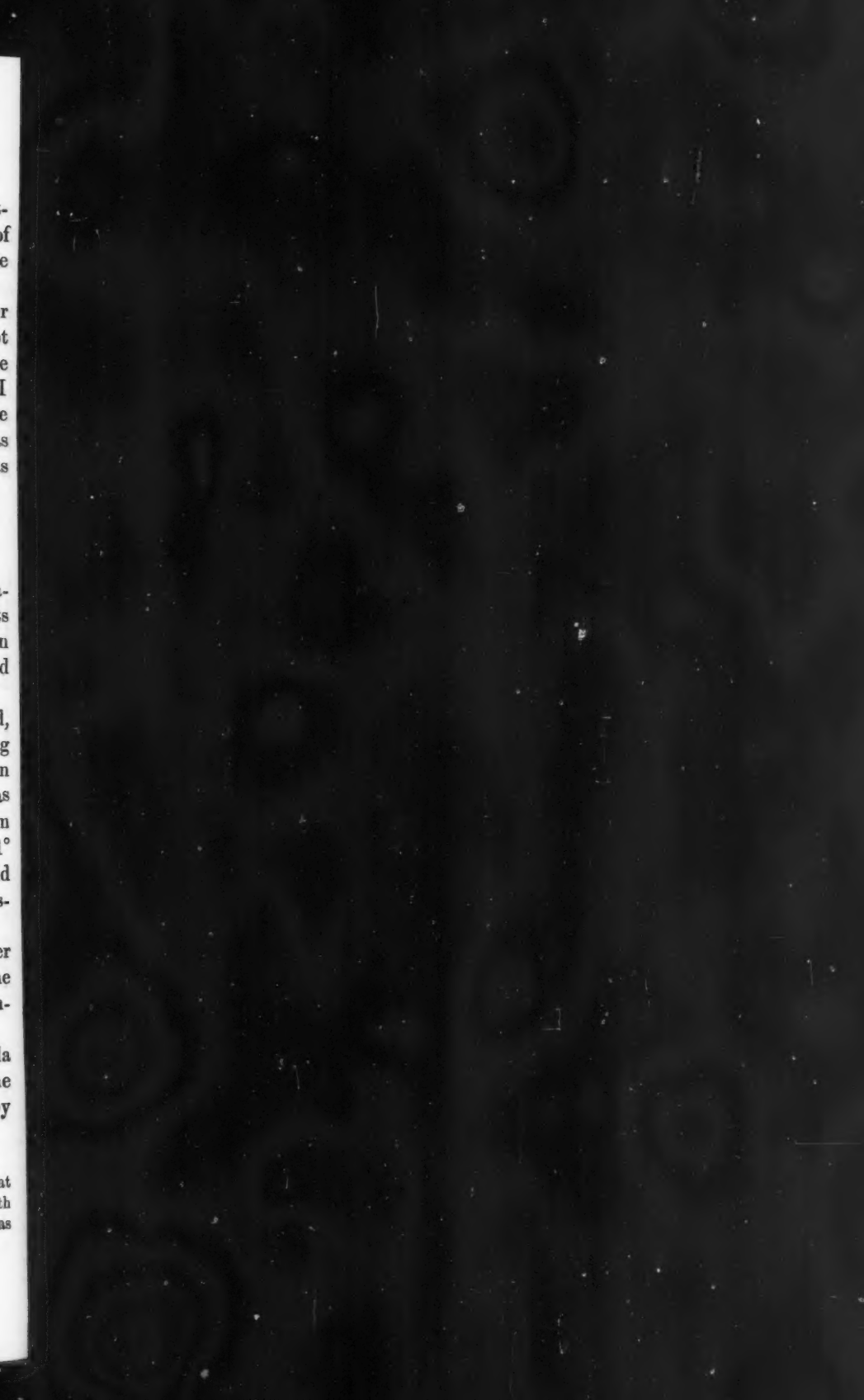
I examined the reaction which takes place with turpentine under these circumstances some years ago, but at that time I was not fully alive to the true explanation, because I had not treated the resulting oil with alcoholic potash or sodium. The analyses I then made indicated the formula of the oil from turpentine to be $C_{20}H_{15}Br.\ 2Br.\ 2HO$. One equivalent of hydrobromic acid was always found in the watery fluid. Assuming this to be correct, as I have no doubt it is, we have

$$C_{20}H_{16}+4Br+2HO=C_{20}H_{15}Br.\ 2Br.\ 2HO+HBr.$$

Every four equivalents of bromine yield, therefore, one equivalent of hydrobromic acid; and in an experiment where 33·2 parts of bromine were employed, 8·2 of hydrobromic acid were found in the aqueous fluid. If the above equation be correct, 8·4 should have been obtained.

The oil produced as above from caoutchin yields, when heated, torrents of hydrobromic acid, and an oil distils over containing less bromine and hydrogen. On cohobating it with sodium in excess, a very fragrant and perfectly colourless hydrocarbon was produced, distilling between 171° and 200°. It was received in four portions: *a*, between 171° and 177°; *b*, 177° to 181°; *c*, 181° to 186°; and *d*, 186° to 200°. A yellowish oil remained behind at this point; it required a very much higher temperature for distillation, and on cooling deposited a few very minute crystals.

Caoutchin and turpentine behave in a precisely similar manner with the above reagents; and it is worthy of observation that the resulting hydrocarbon has the same peculiar odour, from whichever source it is prepared.*

Analysis yielded numbers agreeing completely with the formula $C_{20}H_{14}$, which is that of cymole. Moreover, the density of the liquid, 0·8664 at 20°, was almost the same as that given by Gerhardt, namely, 0·8610 at 14°.

* Since writing the above, I have compared the cymole from caoutchin, and that from oil of turpentine, with a specimen of the same hydrocarbon, prepared with great care from oil of cumin by my friend Mr. Church; the odour in each case was absolutely identical.